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Effect of neutron irradiation on the 1615-cm $^{-1}$ Raman band of polyester fibre

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Abstract : Amorphous polyethylene terephthalate (PET) fibres of denier per filament value 2.17 were irradiated by fast neutron of energy 4.44 MeV at different fluences. The radiation-induced physical, macromolecular changes have been investigated applying micro-Raman scattering. It is observed that the 1615-cm^{-1} band of amorphous PET fibre get vanished at the fluence of 1×10^{11} n/cm^2 indicating the formation of pure *gauche* phase due to radiation heating. This *gauche* phase was also confirmed from the entropy value of irradiated PET material obtained using DSC technique. A *phase-diagram* of amorphous PET was plotted using Raman band intensity and neutron fluence.

Keywords : Polyethylene terephthalate, neutron fluence, Raman scattering

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1. Introduction

Among the synthetic fibres, polyethylene terephthalate (PET) or commonly known as polyester, is significant because of its mechanical strength, inertness to chemical action and resistance to thermal environment. In general, the modification of polymer properties under ionizing radiation [1] is a subject of great interest due to the increasing uses of polymers in various fields like hard radiation environments encountered in nuclear power plants, space-crafts industry, sterilization irradiators, high energy particle accelerators *etc.* Again, PET fibres are mainly used in textile industry [2,3]. Apart from that, it is also used in the field of surgical polymeric textiles [4,5], composites [6,7], nanocomposites [8], conducting polymer [9], electroactive polymer [10] *etc.* Polyesters are mainly cross-linked when irradiated. Cross-linking of macromolecules is facilitated by the appearance of free radical when hydrogen is extracted from the main chain of carbon atoms and can transfer the unpaired electron along the chain. This increases the probability of its proximity to a similar free radical of another macromolecule. At a definite stage of irradiation, the polymer molecules are cross-linked or chemically bonded into a common structure. Then this irradiated polymer possesses the improved mechanical (modulus, hardness, strength *etc.*), electrical, thermal and chemical properties. Neutron irradiation [11-13] significantly changes the properties of polymeric materials by the displacement of lattice atoms and the generation of helium and hydrogen by nuclear transmutation. When fast neutron undergoes an interaction, it does so with a nucleus of the absorbing-material; as a result, materials gain enough energy; hence modification in the material properties takes place. In a head-on collision with hydrogen or hydrogen like materials, the neutron transfers all its kinetic energy in a single encounter. The maximum kinetic energy of the recoil nucleus $(E_R)_{max}$ can be expressed as

$$(E_R)_{max} \quad \frac{4A}{(1+A)^2}$$

where A is the mass of the target nucleus per neutron mass and E_n the kinetic energy of incident neutron. Another important aspect is that the fast neutron can produce dense ionization at deep levels in the material. Such an effect is difficult to be obtained by direct ionization radiation like protons, because it will only produce ionization at the spot, receiving radiation.

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2. Experiment

Partially oriented yarn (POY) of polyethylene terephthalate (PET) fibre used for our investigation was obtained from a commercial polyester plant, which produces the fibre through the following process. Esterification of purified terephthalic acid and ethylene glycol produces oligomer, which is subjected to polycondensation process *via* a 3-stage polycondensation reactor to produce viscous molten PET polymer material. The above hot molten polymer material is allowed to pass through a spinneret where it enters through very fine holes under various machine-setting parameters to produce long PET fibres or POY. The fibre used for the irradiation study is of bright yarn type with raw denier (weight in gram of 9000 meter of yarn) value of 78.2 with 36 filaments. The bright yarn with denier per filament (*dpf*) value 2.17 was used for the irradiation study.

The neutron radiation source used for the present irradiation study was produced from an Am-Be source by (α, η) type nuclear reaction. Taking Am^{241} as a α -source of energy (5.48MeV) an experimental neutron yield of about 70 neutrons per 10^6 α 's is generally obtained from a beryllium target. A neutron beam of energy 4.44 MeV and flux 2.2×10^6 n/ cm^2/s from an Am-Be source was used. According to Nereson and Darden [14] the average energy spread over the 3- to 12-Mev energy range is approximately 10 percent and the over-all accuracy of the results is ±10 percent or better. Spread in neutron energy around 4.4 Mev is approximately 44 keV. The PET fibre samples are irradiate in air at the atmospheric pressure in the temperature range of 22-27 °C for different exposure times to get four different fluences (*i.e.* I to IV) ranging from 1×10^9 n/ cm^2 to 2×10^{11} n/ cm^2. Non-irradiated and irradiated samples were characterized by micro-Raman scattering and Differential Scanning Calorimetry (DSC). For the micro-Raman study, single filaments were taken from the fibre sample and mounted on an amorphous glass plate with double-sided tape at both ends of the filament.

A RAMANOR U 1000, JOBIN YVON, micro Raman setup with a double monochromator designed for high-resolution spectroscopic applications was used for collection of data. The identical monochromators in an additive mount equipped with plane holographic gratings having 1800 grooves/mm are used. Each monochromator features an asymmetric Czerny-Turner mounting equipped with 2 slits open symmetrically. The slit width is manually adjustable from 0-3 mm and has been set at 2 mm. The instrument is equipped with 4 collimating mirrors with independent slit and is mounted on Rayleigh type support for fine and reproducible adjustments. The exit slit of the RAMANOR U 1000 is optically coupled with CCD detector of JOBIN YVON-SPEX Instrument. The experiments were performed using 514.5 nm green line of an argon ion laser source (3 Watts). It was focused to give 160 mW of energy and a 10 μm spot on the surface of the fibre. Raman spectra of single fibres were obtained using a Renishaw 1000 Raman microscope at 180° scattering. Spectral data were accumulated at a fixed grating position and collected using a Peltier-cooled CCD detector. The data acquisition is equipped with SPECTRALINK for scanning and recording the wavenumbers and intensity.

A Netzsch STA 409C simultaneous thermal analyzer which combines simultaneous thermogravimetry and Dynamic Differential Scanning Calorimetry (TG/DSC) with a temperature range of 0 to 1600 °C, was used to measure the mass profile and reaction temperatures of start and end of the reaction of the materials. The thermogravimatry had sensitivity in the order of 1 digit/1.25 micro gram. The experiments were performed in an inert atmosphere (nitrogen atmosphere) with a flow rate of 80ml/ min, operated in the range of 25 °C to 280 °C at a heating rate of 5 K/min. Alumina was used as a standard and the polymer samples of 12-15 mg was taken in an Alumina crucible for the thermal analysis. NETZSCH-TA windows software version 3.5 was used for result analysis.

3. Results

The normalized data of micro-Raman spectra taken from non-irradiated and irradiated single PET filament are shown in Figure 1. In the present investigation, the strongest Raman band [15,16] observed at 1615 cm^{-1} is related to a vibration with C = C starching because of strong aromatic character of PET. Increase in Raman band intensity was observed for initial fluences up to 5×10^{10} n/cm^2, where it is maximum. This increase in Raman band intensity with neutron fluence is probably due to the breaking of the bonds in the molecule because of high-energy radiation heating. Though the change in position of Raman band in PET fibre is stress dependent [17], the contribution of radiation heating microstrain [13] shifts the Raman band towards slightly higher value.

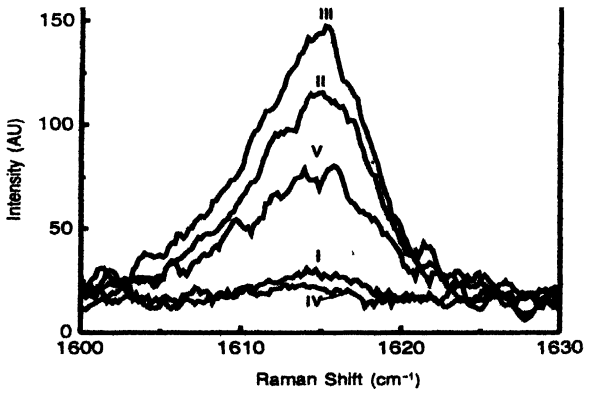

Figure 1. Micro-Raman spectra of non-irradiated or I (virgin) and irradiated like II (1×10^9 n/cm^2), III (5×10^{10} n/cm^2), IV (1×10^{11} n/cm^2) and V (2×10^{11} n/cm^2) PET fibres.

Generally, enhancement of intensity indicates the increase of crystallinity and orientation of molecules. Since the present PET fibre is highly amorphous in nature, the contribution of crystallinity towards the enhancement of band intensity is negligible. So the maximum Raman band intensity observed at fluence 5 × 10^{10} n/cm^2, indicates the maximum orientation of molecules. This was also confirmed by observing lowest (0.053 J/g °C) value of entropy of fusion (*i.e.* ($\Delta H)_f/T_m$, where ($\Delta H)_f$ is enthalpy of fusion and T_m is the melting point) as shown in Figure 2(a) using DSC technique. Again it is interesting to note that the Raman band fully disappears as shown in Figure 2(b) at fluence 1× 10^{11} n/cm^2, indicating the formation of *gauche* phase due to radiation-induced degradation and cross-linking. Observation of the maximum entropy value (*i.e.* 0.33 J/g °C) indicates the high randomization of the PET molecules at the fluence 1× 10^{11} n/cm^2. When the fluence is increased further, the Raman band again appears with less intense and small peak shift as compared to initial fluences. The imperative result of the micro-Raman and DSC are plotted in Figures. 2(a, b). The nature of the curve in Figure 2(b), which is fluence *versus* wavenumber, shows a similar characteristic of the curve plotted between temperature and wavenumber given by Brookes *et al* [15]. There are two parts observed in the curve. It is well known that PET is a two-phase material, the crystalline and amorphous. Along with these crystalline and amorphous, there is a mesomorphic amorphous constituted of *trans* conformers [18]. The crystalline

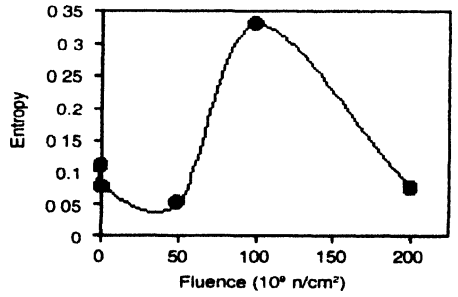

Figure 2. (a) Neutron fluence *versus* entropy of virgin and irradiated samples.

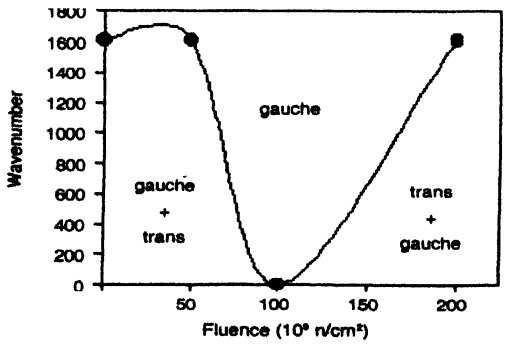

Figure 2. (b) Fluence *versus* wavenumber of irradiated samples.

phase contains bonds that are *trans* because of the ethylene glycol linkage whilst the amorphous region contains both *gauche* and *trans* [19]. A pure amorphous phase constituted solely of *gauche* conformers [18]. Since the present sample is purely amorphous, the virgin sample contains both *gauche* and *trans*. Due to irradiation, the sample gets amorphised and the *trans* amount decreases. In other words, the *gauche* amount increases due to radiation heating. Again, observation of larger entropic contribution confirms the stabilization of *gauche* form [20]. Separation of the *gauche* phase from *trans* + *gauche* are shown in Figure 2(b). It is hoped that by plotting temperature *versus* Raman shift (wavenumber) or fluence *versus* Raman shift, the different phases of polymer can be found *i.e.* a *phase-diagram* can be obtained.

4. Conclusion

The 1615 cm^{-1} Raman band of virgin and 4.44 MeV fast neutron irradiated PET fibres were analysed. From the micro-Raman study, the maximum Raman peak intensity was observed for fluence 5 × 10^{10} n/cm^2 (sample-III) confirming the highest orientation of amorphous fibre molecules. Disappearance of Raman peak intensity at the fluence 1 × 10^{11} n/cm^2 (sample-IV) is indicative of degradation accompanying cross-linking phenomenon. The investigated results in this work, particularly the fibres showing highest orientation (sample-III), are useful for electrical, optical and electroactive applications. Again the cross-linked fibre (*i.e.* sample-IV) is more useful for textile applications and development of polymer composite materials.

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